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Registry No. $[(C_2H_5)_4N]_2Fe(C_5H_4CS_2)_2$, 57918-76-0; $[(C_2H_5)_4N]_3Fe(C_5H_4CS_2)_3$, 57918-78-2.

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Electron Paramagnetic Resonance of Chromium(III) Complexes of the Type *cis*-[Cr(2,2'-bpy)$_2$XY]Z, *cis*-[Cr(1,10-phen)$_2$XY]Z, and *cis*-[Cr(ox)$_2$XY]Z in Frozen Solutions and Powders

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Frozen-solution spectra on X band as well as on Q band have been recorded for three series of Cr(III) complexes of the type *cis*-[Cr(bpy)$_2$XY]Z, *cis*-[Cr(phen)$_2$XY]Z, and *cis*-[Cr(ox)$_2$XY]Z, where XY is H_2O–H_2O, H_2O–OH^-, Cl^-–Cl^-, bpy, phen, ox, en, or acac. For some complexes the Cr-doped powder spectra of the corresponding Co(III) complexes have been recorded. The *D* values of the three series exhibited correlations with the ligand field strengths of the XY ligands. The rhombic distortions of the complexes varied from 0.05 to 0.33 D.

Introduction

This investigation was undertaken in order to provide data about the paramagnetic behavior of cis Cr(III) complexes and to correlate these data with parameters from the visible and ultraviolet spectra. Until now little work has been done on the EPR spectra[1] of cis complexes. On the other hand, various series of trans Cr(III) compounds[2–4] have been investigated. In the case of trans complexes it has become clear that for some series[3] the zero-field parameter *D* depends mainly on the difference of the ligand field strengths of the two substituting ligands on the one hand and the nonsubstituted ligands on the other hand. For other series[2,4] the correlations between *D* and the ligand field strengths are much less convincing. It is assumed that for the most part this is due to the position of the Z principal axis in the complex. In the first case this axis is situated perpendicular to the plane of the nonsubstituted ligands and in the latter case it lies in the plane. For cis Cr(III) complexes as studied in the present investigation, it can be expected that the behavior of the zero-field splitting *D* will reflect the cis substitution with respect to the ligand field strength, but to a smaller degree than in the case of purely tetragonal complexes because the Z axis is not situated in the plane of the XY ligands. Though these cis complexes are not strictly trigonal, they will be treated as such and in this paper will be described as trigonal in order to distinguish them from tetragonal complexes.[36]

Experimental Section

Preparation of Complexes. Most chromium and all cobalt complexes were prepared by established methods.[5–9] The complexes were characterized by means of ir spectroscopy.[9,37] The mixed complex with acetylacetonate, potassium acetylacetonatobis(oxalato)chromate(III) dihydrate, was prepared as follows. A 7.2-g sample of *cis*- or *trans*-$K_2[Cr(ox)_2H_2O(OH)]$[10] in 30 ml of 15% ethanol–water solution was boiled for 15 min with the stoichiometric amount of acetylacetone (2 ml). The green solution turned blue. With $BaCl_2$ in excess, $Ba[Cr(acac)(ox)_2]\cdot 2H_2O$ was precipitated. This compound was treated with the calculated amount of K_2SO_4 in about 10 ml of H_2O. To settle out the $BaSO_4$, the reaction mixture was allowed to stand for 0.5 h on a water bath. The filtrate was cooled to obtain blue-violet crystals of the K salt. Anal. Calcd for $C_9H_7O_{10}CrK_2$: C, 26.6; H, 1.7; O, 39.5. Found: C, 25.9; H, 1.7; O, 40.3.

EPR Spectra. All EPR spectra were recorded on a Varian Model 4052 spectrometer at approximately −160 °C on X band as well as on Q band. The magnetic field strengths were measured with an AEG gaussmeter. The frequency was determined with a Takeda Riken counter, Model 5502A, equipped with a No. 5023 frequency converter. The more soluble compounds were dissolved in a mixture of water, methanol, and dimethylformamide (WMD) of composition 1:8:1. Less soluble compounds were measured in a mixture of 3:4:3 composition by volume.[4]

The pH dependence of the aqua complexes was first established with aqueous solutions of various pH values, frozen in a Sephadex matrix[12] and then compared with the EPR spectra of a 6:2:2 WMD solution with the same pH. It appeared that there were only small differences between the two series, so for analyzing the data WMD frozen solutions were used. The EPR spectrum of *cis*-$[Cr(ox)_2H_2O(OH)]^{2-}$ was recorded in a buffered 6:2:2 WMD solution[34] at pH 8.6, while those of *cis*-$[Cr(bpy)_2H_2O(OH)]^{2+}$ and *cis*-$[Cr(phen)_2H_2O(OH)]^{2+}$ were both recorded[6] at pH 4.7.

The powders were prepared from aqueous solutions of the analogous Co(III) compounds to which 1–2% of the Cr complex was added. The solutions were allowed to crystallize in darkness in order to prevent decomposition.[9] For the measurements only well-shaped crystallites were used. As for K[Cr(ox)$_2$phen], the analogous Co compound could not be prepared; this complex was added to the double complex[9] $[Co(ox)_2phen][Co(ox)(phen)_2]\cdot 3H_2O$. The EPR spectrum showed

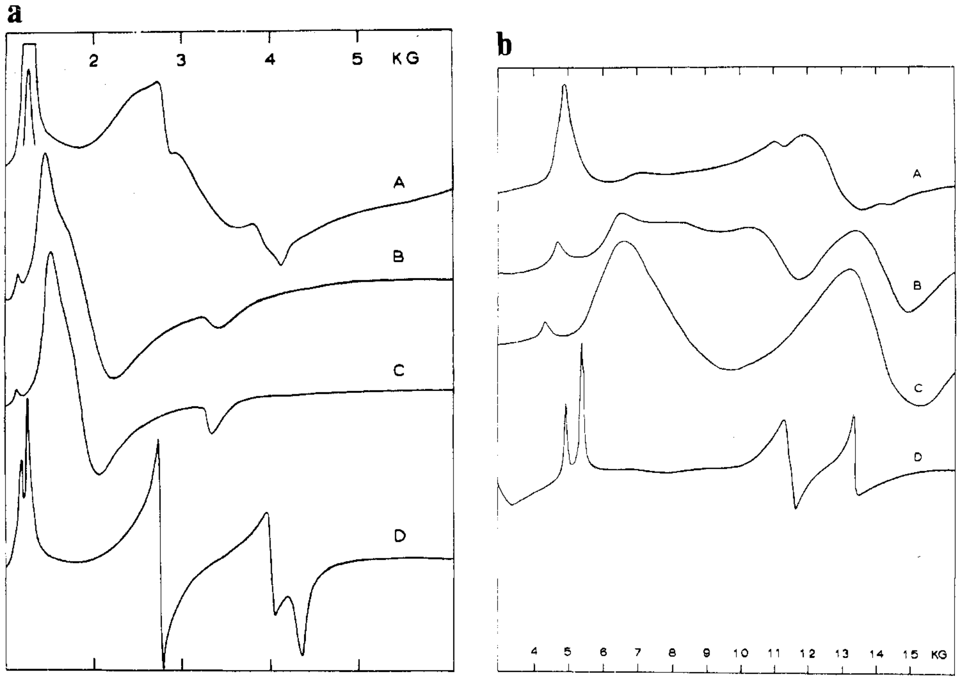

Figure 1. (a) X-Band spectra of *cis*-[Cr(ox)$_2$XY]Z complexes; ν 9050 MHz. (b) Q-Band spectra; ν 35 000 MHz. Curves: A, *cis*-[Cr(ox)$_2$(H$_2$O)$_2$]$^-$ in 1:8:1 WMD, pH 1; superposed on the cis spectrum is the trans spectrum as a result of cis–trans isomerization; B, [Cr(ox)$_2$bpy]$^-$ in 3:4:3 WMD; C, [Cr(ox)$_2$acac]$^{2-}$ in 1:8:1 WMD; D, [Cr(ox)$_2$phen]$^-$ in [Co(ox)$_2$phen][Co(phen)$_2$ox]·3H$_2$O powder.

Table I. Zero-Field Parameters for *cis*-[Cr(ox)$_2$XY]Z in Frozen Solutions

XY	D, cm^{-1}	E, cm^{-1}	WMD
H$_2$O-H$_2$O[a]	0.55 ± 0.01	0.176 ± 0.008	1:8:1
H$_2$O-OH[b]	0.40 ± 0.05	0.13 ± 0.04	6:2:2
bpy	0.66 ± 0.06	0.064 ± 0.006	3:4:3
acac	0.61 ± 0.04	0.038 ± 0.003	1:8:1
en	0.61 ± 0.05	0.11 ± 0.01	3:4:3

[a] pH 1. [b] pH 8.6.

Table II. Zero-Field Parameters for *cis*-[Cr(bpy)$_2$XY]Z in Frozen Solutions

XY	D, cm^{-1}	E, cm^{-1}	WMD
H$_2$O-H$_2$O[a]	0.43 ± 0.03	0.13 ± 0.01	1:8:1
H$_2$O-OH[b]	0.39 ± 0.01	0.11 ± 0.01	6:2:2
Cl-Cl	0.47 ± 0.02	0.107 ± 0.007	1:8:1
ox	0.48 ± 0.02	0.091 ± 0.005	3:4:3

[a] pH 1. [b] pH 4.7.

Table III. Zero-Field Parameters for *cis*-[Cr(phen)$_2$XY]Z in Frozen Solutions

XY	D, cm^{-1}	E, cm^{-1}	WMD
H$_2$O-H$_2$O[a]	0.29 ± 0.01	0.084 ± 0.004	1:8:1
H$_2$O-OH[b]	0.16 ± 0.01	0.054 ± 0.001	6:2:2
Cl-Cl	0.33 ± 0.01	0.055 ± 0.006	3:4:3
ox	0.42 ± 0.09	0.14 ± 0.07	3:4:3

[a] pH 1. [b] pH 4.7.

that no disproportionation of the Cr complex had taken place during crystallization.

Results

All spectra of the investigated compounds are described with the spin Hamiltonian for $S = {}^3/_2$ systems[13]

$$\mathcal{H} = \beta(g_zH_zS_z + g_yH_yS_y + g_xH_xS_x) + D(S_z^2 - {}^5/_4) + E(S_x^2 - S_y^2) \qquad (1)$$

The first term is the magnetic interaction or the Zeeman term; the second and the third ones are the axial zero-field splitting and the rhombic splitting, respectively. In analyzing the spectra it is assumed that the principal axes of the **g** tensor and of the zero-field tensor coincide. In order to assign the peaks in the EPR spectra, diagrams were calculated in which the resonance values of the X, Y, and Z extremes were plotted as a function of the reduced axial zero-field parameter $D/h\nu$, while the value of E/D was given a constant value.[1] For the g factor a value of 1.98 was chosen. By comparing the positions of the experimental peaks with those of the calculated peaks in the diagram an estimate was obtained for the D and E values of the complex. With an automatic computer program the parameters were refined until the sum of the squares of the deviations between the calculated and experimental resonance values became as small as possible.

As a result of peak broadening in EPR frozen-solution spectra of most complexes the resolution of the peaks on X band as well as on Q band was poor, as can be seen in Figures 1–3 in which the X-band and Q-band spectra of the three series

Table IV. EPR Parameters of Cis Chromium Complexes in Powders

Host lattice	D, cm^{-1}	E, cm^{-1}	g_x	g_y	g_z
[Co(ox)$_2$phen][Co(ox)(phen)$_2$·3H$_2$O[a]	0.611 ± 0.002	0.1572 ± 0.0007	1.977 ± 0.006	1.985 ± 0.006	1.982 ± 0.004
K[Co(ox)$_2$bpy]·5H$_2$O (I)[b]	0.572 ± 0.006	0.114 ± 0.002	1.98 ± 0.02	1.97 ± 0.02	1.99 ± 0.02
K[Co(ox)$_2$bpy]·5H$_2$O (II)[b]	0.583 ± 0.003	0.0851 ± 0.0005	1.986 ± 0.006	1.979 ± 0.006	2.003 ± 0.006
[Co(bpy)$_2$ox]Cl·4H$_2$O	0.49 ± 0.01	0.064 ± 0.002	1.98 ± 0.01	1.99 ± 0.01	2.00 ± 0.02
[Co(phen)$_2$ox]Cl·4H$_2$O	0.398 ± 0.001	0.124 ± 0.001	1.989 ± 0.004	1.983 ± 0.004	1.988 ± 0.003

[a] Pure K[Co(ox)$_2$phen] cannot be prepared,[9] so the double complex to which some K[Cr(ox)$_2$phen] was added was used for the powder measurements. [b] All peaks in the powder spectrum are doubled. It is supposed that there are two different sites in the lattice. In analyzing the composed spectrum the D values are taken approximately the same for both sites.

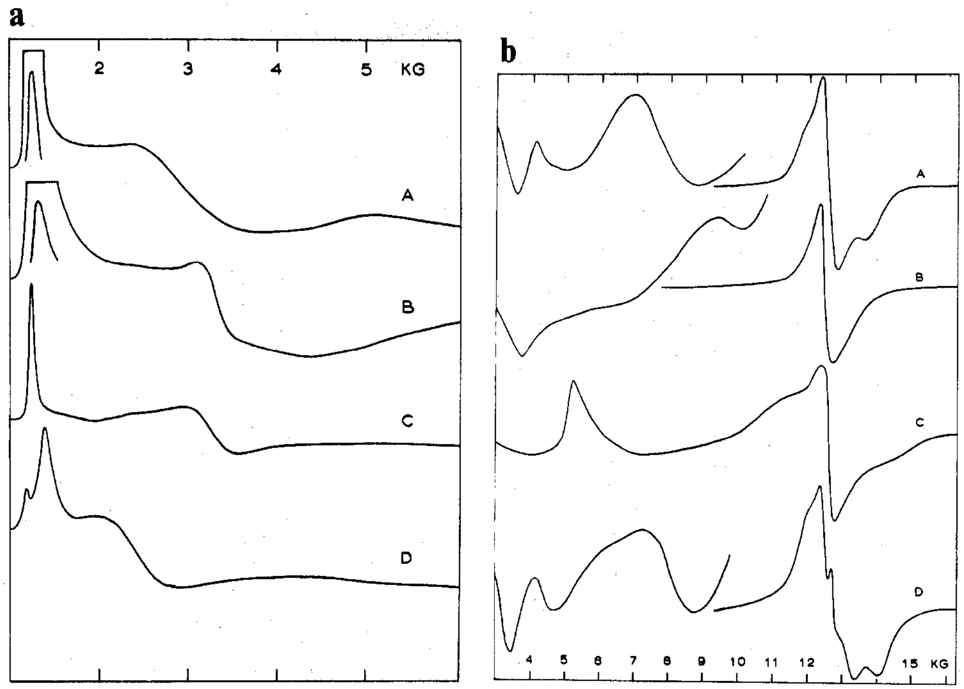

Figure 2. (a) X-Band spectra of *cis*-$[Cr(phen)_2XY]Z$ complexes; ν 9050 MHz. (b) Q-Band spectra; ν 35 000 MHz. At the interruption of the lines the amplification of the signal was reduced with a factor 50. Curves: A, *cis*-$[Cr(phen)_2(H_2O)_2]^{3+}$ in 1:8:1 WMD, pH 1; B, *cis*-$[Cr(phen)_2(H_2O)(OH)]^{2+}$ in 6:2:2 WMD, pH 4.7; C, $[Cr(phen)_2ox]^+$ in 3:4:3 WMD; D, $[Cr(phen)_2Cl_2]^+$ in 3:4:3 WMD.

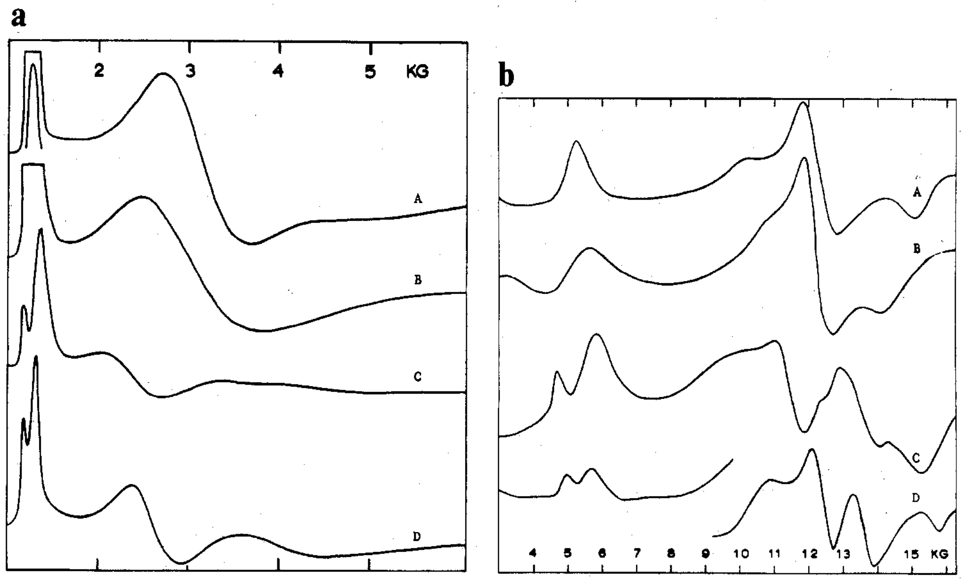

Figure 3. (a) X-Band spectra of *cis*-$[Cr(bpy)_2XY]Z$ complexes; ν 9050 MHz. (b) Q-Band spectra; ν 35 000 MHz. At the interruption of the lines the amplification of the signal was reduced with a factor 50. Curves: A, *cis*-$[Cr(bpy)_2(H_2O)_2]^{3+}$ in 1:8:1 WMD, pH 1; B, *cis*-$[Cr(bpy)_2(H_2O)(OH)]^{2+}$ in 6:2:2 WMD, pH 4.7; C, $[Cr(bpy)_2ox]^+$ in 3:4:3 WMD; D, *cis*-$[Cr(bpy)_2Cl_2]^+$ in 1:8:1 WMD.

of cis Cr(III) complexes are presented. So a parameter fit on only one EPR spectrum was excluded and therefore a fit was performed on the combination of the results of X and Q band. The procedure followed is outlined in Appendix A.

An estimate of the errors in the calculated parameters was obtained by the method of correlated errors by setting up the covariancy matrix. For details of this method one is referred to Appendix B.

The results of the frozen-solution spectra are summarized in Tables I–III. The g values are not given because as a result of the restricted numbers of peaks in the spectra, they could not be determined with an accuracy permitting relevant discussion. The estimated deviations of the g values varied from 1 to 4%. The g values ranged from 1.96 to 2.01. In Table IV the results of the powder spectra are presented. In this table the g values were included because the spectra could be fitted more accurately owing to the number of peaks.

Discussion

For trigonally distorted octahedral complexes many correlations have been performed between the parameters of the visible and ultraviolet spectra and the spin-Hamiltonian parameters of the ground state. Van Vleck[14] has calculated the zero-field splitting (zfs) parameter D by taking into account the splitting of the octahedral $^4T_2$ state as a result of the axial trigonal field. Sugano and Tanabe[15] have pointed out that the $^4T_1$ level also gives a contribution to the zfs through interaction with the ground state. However, the doublet states may not be neglected[16] either in the calculation of the zero-field splitting. Macfarlane[17] has derived analytical expressions up to third-order perturbation for the contributions to the zfs of the various states within the complete d^3 energy matrix. Another study on the trigonal crystal field has been performed by Rimmer and Johnston.[18]

From Macfarlane's work[17] it is concluded that the major contributions to the zfs come from the a^4T_1, a^2T_2, and b^2T_2 levels, while the contribution of the $^4T_2$ level is of minor importance. Since these various states mix in, it is evident that no simple correlation exists between the parameters of the optical spectra and those of the spin Hamiltonian.

A somewhat different approach for these complexes is obtained by the angular overlap model (AOM).[19,20] The one-electron energies are separated into a σ and a π contribution. Furthermore the influence of the nonaxiality of the ligands was taken into account. For tris-bidentate complexes and ortho axially cis-substituted bis-bidentate complexes formulas have been derived[21] for the energy of the quartet states of these complexes in terms of σ and π contributions.

Three different series of complexes have been recorded in order to investigate the variation of the zero-field parameters by substitution on cis positions of the complex. If the experimentally determined values for D, as represented in Tables I–IV, are considered, it can be noticed that for the three series the same sequence of the substituting ligands exists with respect to the D parameter. The observed sequence of D values expressed by the cis substituents is phen > bpy (en) > acac > ox > Cl^- > H_2O > OH^-.

In these series the order of the first three ligands (phen, bpy, en) is not very certain, owing to the large uncertainty of the D values of these cis complexes in frozen solutions. The order of phen and bpy has been taken from the powder spectra. From these series the position of the Cl^- ion between ox and H_2O is remarkable.

If *cis*-MX_4Y_2 complexes are regarded as pseudo *trans*-MZ_4X_2 complexes, then the axial zero-field parameter D can be approximated as $|D| = {}^4/_9\zeta^2|\delta|/\Delta^2$, where ζ is the one-electron spin–orbit constant and $\delta = -{}^5/_2[Dq(X) - Dq(Y)]$ in which $Dq(X)$ and $Dq(Y)$ are the crystal field strengths of the X and Y ligands, respectively. Δ is the energy of the first absorption band ($^4A_2 \rightarrow {}^4T_2$) of the mixed complex. From this it follows that $|D|$ is proportional to $|\delta|$. However, there is no correspondence at all between the order of D values and the calculated order of the crystal field differences $|\delta|$.

An analogous sequence for the ligands is obtained when the so-called field strength Σ is considered. $\Sigma = \Delta/B$, where Δ is the crystal field parameter for octahedral complexes and B is the Racah parameter which represents the interelectronic repulsion. The field strength series for a number of ligands is en (35.5) > NH_3 (33.2) > ox (28.0) > Cl^- (27.5) > H_2O (23.6), the numbers in parentheses denoting the field strengths.[21] As there seems to exist a correlation between Σ and D, an expression for D will be derived as a function of Σ. From the facts that the D values of the investigated *cis*-$[Cr(ox)_2XY]$ complexes do not differ much from that[1] of $K_3Cr(ox)_3$ with $D = 0.77\ cm^{-1}$ and the D values of some *trans*-$[Cr(ox)_2XY]$ complexes were found[4] to be about 1 cm^{-1}, it is assumed that these complexes in first instance may be regarded as trigonal complexes. However, only single-crystal studies can clear up this problem. For almost trigonal complexes ($3|E| \ll |D|$) the formulas derived by Macfarlane[17] may be used to express the zero-field parameter D as a function of Σ

$$D = \left[\frac{2}{9}\frac{v}{D_1{}^2} - \left(\frac{2\sqrt{2}}{3D_1D_4} + \frac{\sqrt{2}}{D_2D_3} + \frac{\sqrt{2}}{D_2D_4} + \frac{\sqrt{2}}{D_3D_4}\right)v'\right]\zeta^2 \quad (2)$$

where $D_1 = E(^4T_2) - E(^4A_2) = \Delta$, $D_2 = E(a^2T_2) - E(^4A_2) = 15B + 4C$, $D_3 = E(b^2T_2) - E(^4A_2) = \Delta + 9B + 3C$, $D_4 = E(a^4T_1) - E(^4A_2) = \Delta + 12B$, ζ is the one-electron spin–orbit constant, B and C are the interelectronic repulsion parameters, $v = -3\langle t_2{}^+|V_{trig}|t_2{}^+\rangle$, and $v' = \langle t_2{}^+|V_{trig}|e^+\rangle$. In D_4 the interaction between the a^4T_1 and b^4T_1 levels has been neglected. v and v' are defined following Pryce and Runciman.[22] In eq 2 only second-order contributions have been included.

If formula 2 is expressed in the field strength Σ and if the assumption $C = 4B$ is made (which for most Cr complexes is a reliable value[27] but if another choice is made the conclusions are not affected very much), then the expression for the zero-field splitting becomes

$$D = v'\left[\frac{2}{9}\frac{v}{v'\Sigma^2} - \left(\frac{2\sqrt{2}}{3\Sigma(\Sigma + 12)} + \frac{\sqrt{2}}{31(\Sigma + 21)} + \frac{\sqrt{2}}{31(\Sigma + 12)} + \frac{\sqrt{2}}{(\Sigma + 21)(\Sigma + 12)}\right)\right]\left(\frac{\zeta}{B}\right)^2 \quad (3)$$

or

$$D = v'Z(\zeta/B)^2 \quad (4)$$

From eq 3 and 4 it can be seen that Z depends on Σ and v/v'. The range of experimentally determined absolute values of the ratios[23,24] of v and v' lies between 0.5 and 2. Therefore in the calculations the ratio of v/v' is set equal to 1. If various values of Z are calculated within the range of Σ values between 25 and 35, it follows that for increasing Σ the absolute values of Z and as a consequence those of D decrease. This behavior is not observed experimentally within the series.

For good reasons it can be supposed that the ratio ζ/B for the various complexes does not change very much. B as well as ζ can be described as a function of $\langle r^{-1}\rangle$,[25] which in turn is a function of the charge of the Cr atom. Now it is assumed that for the various complexes the effective charges on the chromium atom do not differ very much, so the variations in ζ/B will be small compared with those in Z. Hence the product $Z(\zeta/B)^2$ still decreases with increasing Σ.

So it concluded that the most important contribution to the variation in the zero-field splitting arises from v'. However, very few data are available about values[35] of v'. For Cr^{3+} in ruby[18,23] $v' = 400\ cm^{-1}$ and for $[Cr(ox)_3]^{3-}$ in $NaMg[Cr(ox)_3]\cdot 9H_2O$ a value of 1760 cm^{-1} for v' has been determined.[24] In GASH (guanine aluminum sulfate hexahydrate) a value of 1800 cm^{-1} is found.[26] For $[Cr(ox)_3]^{3-}$ with eq 3 for $|D|$ a value of 0.53 cm^{-1} is calculated. However, for the *cis*-$[Cr(ox)_2XY]$ series no values for v and v' have been determined so that it is impossible to check eq 3 for these complexes. Moreover, detailed information about the v' values of the investigated bpy and phen complexes is hard to obtain as a result of the charge-transfer bands which obscure the $^4T_1$ bands of the spectra. Further covalency effects[28] in the trigonal distortion can influence the effective splittings of the bands.

If the D values of the analogously substituted complexes are compared between the three series, it is observed that the values of D always have the sequence $Cr(ox)_2XY$ > $Cr(bpy)_2XY$ > $Cr(phen)_2XY$. This order apparently demonstrates the influence of Σ as a result of different $Cr(AA)_2$ skeletons, where AA = ox, bpy, or phen.

The rhombic distortion parameter E does not behave as regularly as the axial parameter D, especially not for the $[Cr(phen)_2XY]Z$ complexes. With some reserve it can be concluded from the experimentally determined values from Tables I–IV that E behaves inversely proportional to the field strength Σ of the substituting ligand. However, the sequence of H_2O–H_2O and H_2O–OH^- is permuted for all complexes. The value of the rhombic splitting depends on the splitting of the ^4E and ^2E levels as a result of the lower symmetry component. No explicit formulas for E have been derived for an octahedron with an axial field of trigonal symmetry and a rhombic distortion.

The values of the ratio E/D for the H_2O–H_2O and H_2O–OH^- complexes of the three series are all close to ${}^1/_3$.

It can be shown that the maximum value of E/D equals $^1/_3$,[30] so these complexes exhibit very large rhombic distortions. It is possible that part of these distortions is caused by hydrogen bonding with the solvent molecules. Also the presence of one nonbonded lone pair on the H_2O molecule and two on the OH^- ion gives rise to considerable nonaxial distortion of the crystal field.

For $[Cr(ox)_3]^{3-}$ the zero-field splittings have been studied in several lattices.[1,31-33] From these studies it followed that the D values were less affected by the lattice than the E values. From a frozen-solution spectrum and an anhydrous powder spectrum[1] it followed that the rhombic distortion of this tris-bidentate Cr(III) complex was very small (about 0.015 cm^{-1}). Substitution of one oxalate ligand by a different one reduced the D value and sometimes considerably enhanced the E value. The more the substituting ligand differed from the substituted ligand with respect to the field strength as well as to the geometry the more the E value changed. So substitution of an oxalate by an acac ligand did not change either D or E very much, while introduction of en or bpy enhanced E much more.

Attempts have been made to include the zfs values of the dihydroxy complexes into the series as well, but the results did not seem very reliable, because all EPR spectra indicated very low zero-field splittings. It is to be expected that the D values of the OH^-–OH^- complexes will be somewhat lower than those of the corresponding H_2O–OH^- complexes, but not much lower. The results are probably obscured by decomposition of the chromium complexes into chromium hydroxide or related compounds. Chromium hydroxide is nearly octahedral and possesses a very low D value, which should be comparable with the D value of about 0.01 cm^{-1} for $[Cr(H_2O)_6]^{3+}$. The frozen solution spectrum of such a complex is very intense in the region of $H_{res} = h\nu/g\beta$, because all transitions are situated within a very narrow field range and all coincide as a result of line broadening. A few percent of the hydroxide complex can completely obscure the spectrum of the real *cis*-dihydroxy complex. Another possibility that can influence the recorded spectra is the formation of an oxygen-bridged binuclear chromium complex as a result of adding OH^- in excess to solutions of the diaqua complexes. In order to establish that the observed spectra were not due to bridged complexes, di-μ-hydroxo-bis[bis(2,2'-bipyridine)chromium(III)] perchlorate was prepared[11] and the EPR spectrum of a frozen solution was recorded. However, this spectrum did not resemble that of the compound prepared in excess OH^-. So this possibility must be ruled out.

The D values of the powder spectra as represented in Table IV do correspond with those of the frozen solutions. The agreement of the E values is less satisfactory. However, for powders it must be expected that there is also an important influence of the lattice, which will affect the rhombic distortion more strongly than the axial one.

From the estimations of the errors of the parameters it was concluded that the ratio E/D could be fitted very accurately in spite of the small number of data. This results from the fact that E/D more strongly determines the relative positions of the first peaks than the values of D (if $D/h\nu$ is larger than 0.5). In most cases the inaccuracy is probably smaller than those reported in Tables I–IV wherein the fit was only made on the extrema with X, Y, or Z principal axis parallel to the magnetic field, but often there are other peaks due to interaxial maxima, especially in Q-band spectra. If these peaks are included too in the calculations, a reduction of the errors will be the result. As the derivatives with respect to the various parameters are difficult to calculate, they were omitted. From the covariancy matrices it is concluded that the correlation between D and E is large. Between the zero-field parameters and the g values the correlation is moderate, and as can be expected the correlation between the separate g values is only small.

Conclusions

From this investigation on cis-substituted trigonally distorted Cr(III) complexes it appeared that the axial zero field parameter D could be correlated with the field strength of the substituting ligand. The magnitude of D was shown to be a function of the matrix elements v' and v of the trigonal field between the two octahedral sublevels e^+ and t_2^+ ($v' = \langle e^+|V_{trig}|t_2^+\rangle$, $v = \langle t_2^+|V_{trig}|t_2^+\rangle$). Owing to a lack of sufficient data for v and v' no quantitative results could be achieved. The rhombic distortion parameter E was influenced considerably by cis substitution.

Appendix A. Automatic Fitting Procedure for EPR Parameters of Powder or Frozen-Solution Spectra at Two or More Frequencies

In order to perform these fittings eq 1 is divided by $h\nu$, the energy of the irradiated microwave quanta. The zero-field parameters are expressed in the dimensionless quantities $D/h\nu$ and $\kappa = E/D$. The magnetic field is written as $H/h\nu$. To obtain the magnetic resonance values the secular determinant is solved[1] for various frequencies at which the spectra were recorded by simply changing the $D/h\nu$ values in the appropriate way. This is the only parameter that depends on the frequency. By comparing the calculated resonance values with the experimentally determined ones the sum of the squares of the differences is made as small as possible by changing the parameters by little steps. The rate of convergency depends largely on a good initial choice of the parameters.

Appendix B. Estimation of the Errors in the Parameters Obtained from Powder or Frozen-Solution Spectra

In order to get an impression about the reliability of the parameters calculated from randomly oriented paramagnetic species a method was used which depends on the calculation of the covariancy matrix. The following procedure can also be used when the results of the spectra for two or more frequencies are combined. It is assumed that in the neighborhood of a calculated field resonance value deviations in the magnetic field can be expressed linearly in the EPR parameters

$$dH = \left(\frac{\partial H}{\partial D}\right)_0 dD + \left(\frac{\partial H}{\partial E}\right)_0 dE + \left(\frac{\partial H}{\partial g_x}\right)_0 dg_x + \left(\frac{\partial H}{\partial g_y}\right)_0 dg_z + \left(\frac{\partial H}{\partial g_z}\right)_0 dg_y \qquad (5)$$

The derivatives in eq 5 are determined for the calculated parameters by implicitly differentiating the resonance condition. For the combination of the results for two or more frequencies eq 5 must be expressed in relative quantities. The zero-field parameters are written in the dimensionless quantities $D/h\nu$ and κ ($=E/D$), while the magnetic field strengths are divided by $h\nu$. We obtain the equation

$$\frac{dH/h\nu}{H/h\nu} = \left(\frac{\partial H/h\nu}{\partial D/h\nu}\right)_0 \left(\frac{D/h\nu}{H/h\nu}\right)\left(\frac{dD/h\nu}{D/h\nu}\right) + \left(\frac{\partial H/h\nu}{\partial \kappa}\right)_0 \left(\frac{\kappa}{H/h\nu}\right)\left(\frac{d\kappa}{\kappa}\right) + \sum_i \left(\frac{\partial H/h\nu}{\partial g_i}\right)_0 \left(\frac{g_i}{H/h\nu}\right)\left(\frac{dg_i}{g_i}\right) \quad (i = x, y, z) \qquad (6)$$

Or, equating the observed differences with the derivatives of eq 6, we get

$$\frac{\Delta H}{H} = f_D\left(\frac{\Delta D}{D}\right) + f_\kappa\left(\frac{\Delta \kappa}{\kappa}\right) + \sum_i f_{g_i}\left(\frac{\Delta g_i}{g_i}\right) \quad (i = x, y, z) \qquad (7)$$

In eq 7 the factors f_D, f_κ, and f_{g_i} are regarded as weight factors. Squaring eq 7, the contributions to the matrix elements of the normal equation are obtained for a particular resonance condition. Summing up all of the contributions of the various resonance conditions of the EPR spectra a symmetric matrix (I) is obtained. The summation runs over the number n of

$$\begin{array}{cccccc} & \Delta D/D & \Delta\kappa/\kappa & \Delta g_x/g_x & \Delta g_y/g_y & \Delta g_z/g_z \\ \dfrac{\Delta D/h\nu}{D/h\nu} & \Sigma f_D{}^2 & \Sigma f_D f_\kappa & \Sigma f_D f_{g_x} & \Sigma f_D f_{g_y} & \Sigma f_D f_{g_z} \\ \Delta\kappa/\kappa & & \Sigma f_\kappa{}^2 & \Sigma f_\kappa f_{g_x} & \Sigma f_\kappa f_{g_y} & \Sigma f_\kappa f_{g_z} \\ \Delta g_x/g_x & & & \Sigma f_{g_x}{}^2 & \Sigma f_{g_x} f_{g_y} & \Sigma f_{g_x} f_{g_z} \\ \Delta g_y/g_y & & & & \Sigma f_{g_y}{}^2 & \Sigma f_{g_y} f_{g_z} \\ \Delta g_z/g_z & & & & & \Sigma f_{g_z}{}^2 \end{array} \qquad \text{(I)}$$

experimental resonance values included in the calculation. If the inverted matrix I is multiplied by $(\sum(\Delta H/H)^2)/(n - 5)$ then the covariancy matrix is obtained. The roots of this matrix give the relative errors of the parameters. The nondiagonal elements give the covariancies between the parameters. The denominator $(n - 5)$ gives the number of independent normal equations (i.e., the number of observations minus the number of parameters).

Registry No. *cis*-$[Cr(ox)_2(H_2O)_2]^-$, 15489-30-2; *cis*-$[Cr(ox)_2(H_2O)(OH)]^{2-}$, 53992-86-2; *cis*-$[Cr(ox)_2bpy]^-$, 21748-32-3; *cis*-$[Cr(ox)_2acac]^{2-}$, 57620-63-0; *cis*-$[Cr(ox)_2en]^-$, 21827-84-9; *cis*-$[Cr(ox)_2phen]^-$, 21748-33-4; *cis*-$[Cr(bpy)_2(H_2O)_2]^{3+}$, 36513-26-5; *cis*-$[Cr(bpy)_2(H_2O)(OH)]^{2+}$, 57651-38-4; *cis*-$[Cr(bpy)_2Cl_2]^+$, 27803-22-1; *cis*-$[Cr(bpy)_2ox]^+$, 32629-19-9; *cis*-$[Cr(phen)_2(H_2O)_2]^{3+}$, 47667-82-3; *cis*-$[Cr(phen)_2(H_2O)(OH)]^{2+}$, 57651-39-5; *cis*-$[Cr(phen)_2Cl_2]^+$, 27803-06-1; *cis*-$[Cr(phen)_2ox]^+$, 32626-76-9.

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Electrochemical Properties of Cobalt(II) Complexes of the Tridentate Ligands Tri(2-pyridyl)amine, Tri(2-pyridyl)phosphine, Tri(2-pyridyl)phosphine Oxide, and Tri(2-pyridyl)arsine[1]

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The electrochemical properties of the Co(II) complexes of the tridentate ligands tri(2-pyridyl)amine (TPAm), tri(2-pyridyl)phosphine (TPP), tri(2-pyridyl)phosphine oxide (TPPO), and tri(2-pyridyl)arsine (TPAs) have been investigated in acetonitrile. It was found that in the complexes $[Co(TPX)_2](ClO_4)_2$ and $Co(TPX)(NO_3)_2$, TPP, TPPO, and TPAs will yield a stable one-electron reduction product while TPAm will not. A one-electron oxidation was observed for the $[Co(TPX)_2](ClO_4)_2$ complexes in which TPX is TPAm, TPP, or TPAs. No oxidation waves were observed for $[Co(TPPO)_2](ClO_4)_2$ or for any of the $Co(TPX)(NO_3)_2$ complexes. Mixed complexes of the type $[Co(TPX)(TPY)](ClO_4)_2$ (TPX ≠ TPY) were prepared by the reaction of $Co(TPX)(NO_3)_2$ with TPY. Only electrochemical means were able to show conclusively that a mixed complex had formed.

Introduction

Metal(II) perchlorate and metal(II) nitrate complexes with tri(2-pyridyl)phosphine (TPP), tri(2-pyridyl)phosphine oxide (TPPO), and tri(2-pyridyl)arsine (TPAs) of the composition $[M(TPX)_2](ClO_4)_2$,[2] $[M(TPX)_2](NO_3)_2$, and $M(TPX)(NO_3)_2$[3] (TPX is one of the above ligands and M is Mn, Co, Ni, Cu, or Zn) have previously been reported. Coordination of the ligands occurs in a tridentate manner through the pyridyl nitrogens with no indication of coordination by the ligand central atom. The coordination sphere of the metal contains six pyridyl groups and may be compared to $[M(py)_6]^{n+}$, $[M(bpy)_3]^{n+}$, $[M(phen)_3]^{n+}$, and $[M(terpy)_2]^{n+}$ (py is pyridine, bpy is 2,2'-bipyridine, phen is 1,10-phenanthroline, and terpy is 2,2',2''-terpyridine). Numerous complexes containing py, bpy, phen, and terpy have been reported and for the latter three ligands, reduced species with the metal ion in a formal oxidation state of +1, 0, or −1 have been observed.[4-12] It is generally concluded that these ligands stabilize formal low oxidation states of metal ions by their ability to accept electrons via a $t_{2g} \rightarrow \pi^*$ back-bonding mode.[13] The $[M(py)_6]^{n+}$ complexes also have this type of backbonding available, yet there are no reports that pyridine stabilizes low oxidation states

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